

ANALYSIS OF THE n-HEPTANE SOLUBLE FRACTION OF COAL HYDROGENOLYSIS PRODUCTS BY HPLC

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Liquid products from the hydrogenolysis of coal are very complex and time and cost constraints limit the detail to which they can be characterized. Methods have been developed to separate the complex liquids into classes of chemical compounds and average properties of such fractions are often reported. Many of the separation schemes are adapted from methods applied to petroleum. Solvent extraction has been widely used to separate the liquid into hexane-soluble oils, asphaltenes and pre-asphaltenes (1). Liquid chromatography using ion exchange and clay columns has been used to separate coal liquids (2,3). Neutral oils were further fractionated on columns packed with silica and alumina to produce saturate, 1-ring aromatic, 2-ring aromatic and polynuclear aromatic fractions. Sequential elution by solvents allows separation into a larger number of fractions (4,5).

High performance liquid chromatography (HPLC) offers the potential for detailed yet rapid separation of complex liquid mixtures. Both solvent and column packing can be varied to give the desirable separation. In this research, the heptane soluble fractions from the heavy oil produced by hydrogenolysis of coals have been separated by HPLC and characterized by various analytical methods.

Experimental

The coal-derived liquid samples were obtained from the hydrogenolysis of coals in an entrained-flow reactor (6,7). The reaction was catalyzed with 6% ZnCl_2 at approximately 500°C and 12.4 MPa hydrogen pressure. The residence time varied from 20 seconds to 12 minutes depending on the properties of the coal. Seven samples from the study of Garr (6) were selected, as well as one medium volatile bituminous coal. Properties of the coals are listed in Table 1 (6,8). Coals were selected which showed a range of reactivity during hydrogenolysis. The yield of products and the properties of the heptane-soluble fraction are found in Table 2. Conversion is defined as one minus the toluene insoluble fraction. The heavy oil is defined as the material collected in the first condenser of the liquefaction reactor. It consists of the liquids transported in the vapor phase from the hot catch tank, boiling above approximately 100°C . The heavy liquid was extracted in Soxhlet apparatus to obtain the heptane soluble fraction.

The heptane soluble fraction was separated by two HPLC schemes. A Waters modular HPLC system was used with two solvent delivery systems, a solvent programmer, an automated sample injector, a UV absorbance detector, a differential refractometer detector, and a data module. The first scheme employed an NH_2 - μ Bondapak column. Saturates and non-polar aromatics were eluted with heptane at a flow rate of 2.0 ml/min. After 15 minutes, flow was reversed and a polar fraction was eluted. After 45 minutes, a 90/10 mixture of $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ was introduced to elute a more polar fraction. This method is similar to that employed by Dark and McFadden (9). The second scheme employed a phenyl- μ Bondapak column and a non-linear gradient. The initial solvent was n-heptane. The gradient involved a 90/10 mixture of $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ mixed with the heptane up to 75% over 36 minutes. A non-polar fraction was eluted by the heptane and a polar fraction was eluted by the gradient.

The heptane-soluble fractions were analyzed by carbon, hydrogen and nitrogen analysis and by vapor pressure osmometry (VPO). A Perkin-Elmer Model 240 CHN analyzer was used for elemental analysis. The VPO measurements were performed in dilute pyridine solutions.

The fractions collected by HPLC separations were analyzed by gas chromatography/mass spectrometry. A 3% Dexsil 300 on Supelcoport was used for the separation. Approximately 300 mass spectral scans were recorded for each sample. Total ion chromatograms were obtained. Mass chromatograms were obtained for selected fragment masses. The fractions were also analyzed by Fourier Transform infrared techniques.

Results and Discussion

The conversion of the coal to toluene-soluble liquids, water and gases varies from 26% to 86%. The low conversion sample 7 is a lower rank coal and the conversion is mostly due to pyrolysis rather than hydrogenolysis. The residence time of this sample was only 20 seconds, indicating that the sample was blown through the reactor with little reactions. Samples which soften and agglomerate are retained in the reactor for longer times and show greater conversion. A sample with high conversion will pass through the reactor in 2-5 minutes while sample 6 required 12 minutes.

The molecular weight of the heptane-soluble fractions is about 285 and is independent of the degree of conversion or the properties of the starting coals. The hydrogen-to-carbon ratios vary from 1.08 to 1.41. The lower number corresponds to the medium volatile coal, which has a lower H/C ratio than the other coals. These values are averages for the entire fraction and do not indicate the range covered by the sample. More detailed analysis of a sample similar to No. 3 indicated a range of molecular weights of from 200 to 700 and the H/C ratio varied from 0.8 to 1.5 (10).

HPLC separation with the NH_2 - μ Bondapak column produces a non-polar fraction that is eluted with heptane, a polar fraction that is adsorbed on the column and is eluted with heptane by reversing the direction of flow and a more strongly adsorbed fraction that is only removed by a polar solvent. Only the first fraction shows chromatographic separation. The elution pattern for each of the eight samples is very similar, differing only in the relative amounts of the three fractions.

HPLC separation with the phenyl- μ Bondapak column produces a non-polar fraction which elutes with heptane and a solar fraction that elutes with the increasingly polar solvent gradient. Samples 4, 6 and 8 showed considerable material eluting between the two fractions. The other samples showed only the two, rather distinct peaks. The phenyl- μ Bondapak column offers the potential for improved separations of the liquids.

The infrared spectra of all non-polar fractions are similar. They show moderate OH stretching near 3400 cm^{-1} and some C=O stretching at 1700 cm^{-1} . The aromatic C-H stretch is weak but there are bands due to aromatic species at 1600 cm^{-1} and 800 cm^{-1} and aliphatic compounds at 1455 cm^{-1} . The polar compounds show a stronger OH absorption and lower carbonyl intensities. The spectra of all polar fractions are similar.

The GC/MS results demonstrate that the non-polar fractions contain alkyl aromatics. The aromatic systems are highly substituted with alkyl chains and saturated rings. The polar groups contain phenols and diphenols in addition. These results agree with previous structural characterization of coal liquids (10, 11,12).

The HPLC separation offers the potential for separating and characterizing coal-derived liquids. However, the samples analyzed in this study did not show major differences, even though they were produced from different coals with different degrees of conversion.

References

1. M. J. Mina, H. Schultz and W. F. McKinstry, Analytical Methods for Coal and Coal Products, Vol. 1, C. Karr, Jr., Ed., Academic Press, New York, 1978, p. 557.
2. J. E. Dooley, G. P. Sturm, Jr., P. W. Woodward, J. W. Vogh and C. J. Thompson, "Analyzing Syncrude from Utah Coal," Bartlesville Energy Research Center, Rept., BERC/RI 7517, August 1975.
3. S. W. Holmes, P. W. Woodward, G. P. Sturm, Jr., J. W. Vogh and J. E. Dooley, "Characterization of Coal Liquids Derived from the H-Coal Process," Bartlesville Energy Research Center Rept., BERC/RI 7610, November 1976.
4. M. Farcasiu, Fuel, 56, 9 (1977).
5. M. Farcasiu, T. O. Mitchell, D. D. Whitehurst, Am. Chem. Soc., Fuel Chem. Div., Preprints, 21(7), 11 (1976).
6. G. Garr, "The Quality of Utah Coals for Synthetic Fuels Production," M.S. Thesis, University of Utah, 1978.
7. G. T. Garr, J. M. Lytle and R. E. Wood, Fuel Proc. Tech., 2, 179 (1979).
8. R. E. Wood and D. M. Bodily, Am. Chem. Soc., Fuel Chem. Div., Preprints, 24(2), 364, (1979).
9. W. A. Dark and W. H. McFadden, J. Chromatogr. Anal., 16, 289 (1978).
10. S. Yokoyama, D. M. Bodily and W. H. Wiser, Am. Chem. Soc., Div. Fuel Chem., Preprints, 21(7) 84 (1976). Accepted for publication in Fuel.
11. S. Yokoyama, D. M. Bodily and W. H. Wiser, Fuel, 58, 162 (1979).
12. S. Yokoyama, N. Tsuzaki, T. Katoh, Y. Sanada, D. M. Bodily and W. H. Wiser, in Coal Structure, M. L. Gorbaty and K. Ouchi, Eds., Adv. Chemistry, Series 192, Am. Chem. Soc., Washington, D.C., 1981, p. 257.

Table 1
Properties of Coals^a

Sample No.	Coal, Field	Volatile matter, % mafb	H/C	Vitrinite reflectance, %	Inert macerals, %	Rank
1	Beehive, Wasatch Plateau	53.6	0.93	0.556	8.5	HVAB
2	Swisher, Wasatch Plateau	52.3	0.90	0.533	4.5	HVAB
3	Hiawatha, Wasatch Plateau	50.3	0.93	0.547	4.1	HVAB
4	Kaiser, Book Cliff	43.9	0.84	0.714	6.7	HVAB
5	Soldier Creek, Book Cliff	49.2	0.82	0.658	20.7	HVAB
6	Convulsion Canyon, Salina	45.3	0.85	0.502	35.5	HVAB
7	Morby Seam, Coalville	59.0	0.84	0.527	18.1	HVCB
8	Coal Basin (Colorado)	26.0	0.71	--	--	MVB

^a

Data for Samples 1-7 from Reference 6.
Sample 8 from Reference 8.

Table 2
Hydrogenolysis Products

Sample	Conversion, ^a % coal	Heavy oil, ^a % coal	Heptane Soluble Fraction		
			% of Heavy oil	Molecular weight	H/C
1 ^b	86.2	67.4	59.0	298	1.34
2	71.0	53.4	47.1	280	1.32
3	79.6	55.3	71.3	289	1.30
4	73.5	60.0	43.3	284	1.39
5	37.3	20.3	49.7	293	1.28
6	53.3	37.8	65.8	280	1.22
7	26.3	7.1	66.7	286	1.41
8	47.5	28.9	53.9	273	1.08

^a

Data from Reference 6.

^b

3% ZnCl₂.